# Kinetics versus Equilibrium

Kinetics: speed of the reaction, how fast or slow the reaction happens

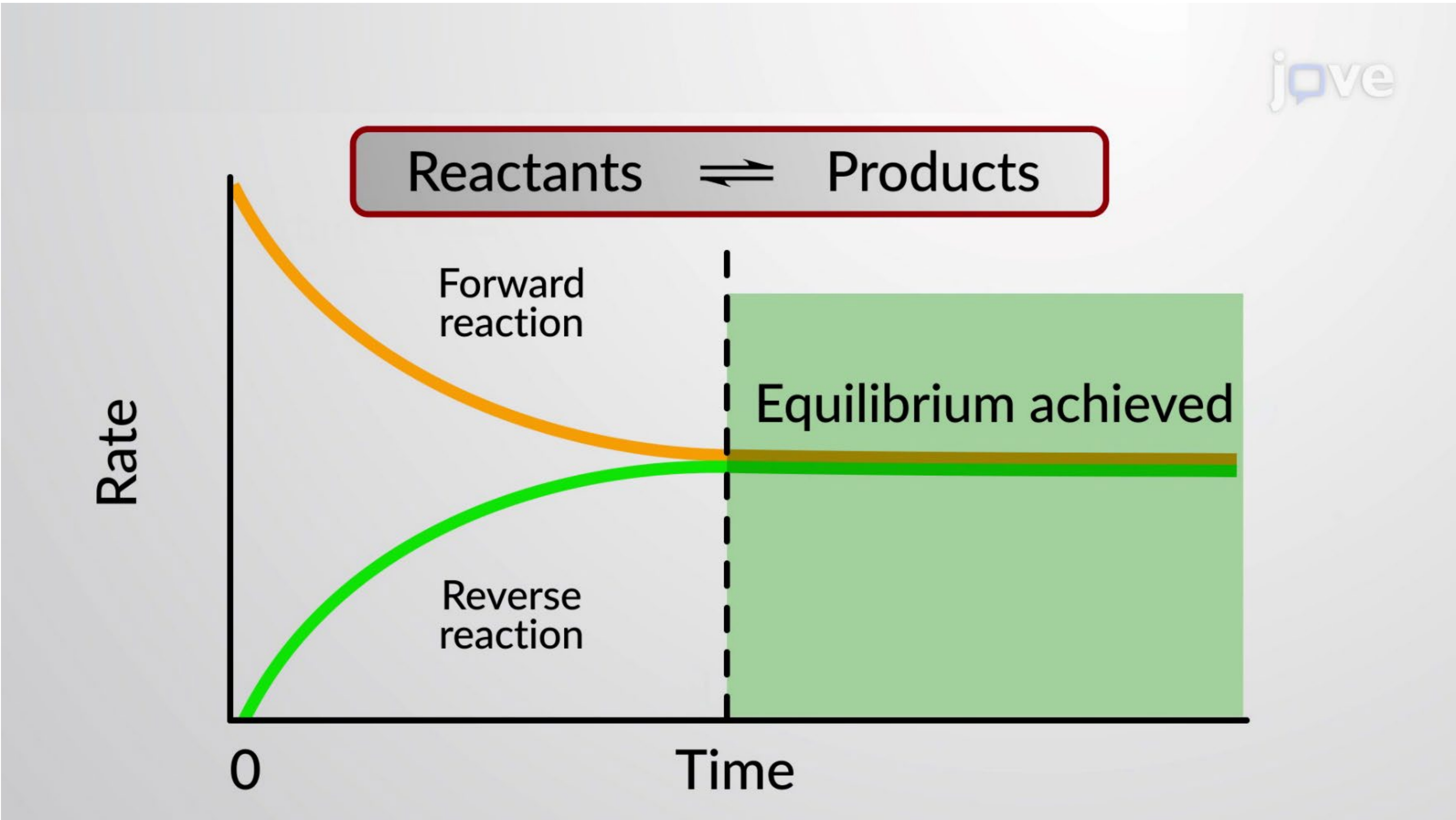
Equilibrium: does not say anything about how fast the rxn. proceeds; $\rightleftharpoons$

- whether the reaction @ $\rightleftharpoons$ is reactant or product favored

@ $\rightleftharpoons$ rate for = rate rev.

At equilibrium

rate forward reaction = rate of reverse reaction




Derivation of equilibrium constant (Keq)

ⓐ ⇌ ratefor = raterev

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

$$\frac{k_f [A]^a [B]^b}{k_r [C]^c [D]^d} = \frac{k_r [C]^c [D]^d}{k_r [C]^c [D]^d}$$

"new" term

$$K_{eq} = \frac{k_f}{k_r}$$

$$\frac{k_f}{k_r}\left(\frac{[A]^a [B]^b}{[C]^c [D]^d}\right) = 1$$

$$K_{eq}\left(\frac{[A]^a[B]^b}{[C]^c[D]^d}\right) = 1$$

$$\therefore K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

"unitless"

if $K_{eq} > 1$ product favored @ eq

$$aA + bB \rightleftharpoons cC + dD$$

if $K_{eq} < 1$ reactant favored @ eq

$K = 1$ neither reactant or product favored

# Writing equilibrium expressions

- **Solids and liquids are not included in equilibrium expression!**

only including gases or aq. solutions

- **Write equilibrium expression for the following eq reactions**

$PV = nRT$

gases can measure partial pressure or concentration, M

$P = \frac{n}{V} RT$

- If K is > 1 the reaction is product or reactant favored?

- If K<1 the reaction is reactant or product favored

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{3}^{2-}{}_{(aq)}$$

$$K_{eq} = [Ca^{2+}][CO_3^{2-}]$$

$K_{c}$ * use molarity

$K_{p}$ * use pressure

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

write an equilibrium expression, Kc.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

write for $K_p$

$$K_p = \frac{P_{NH_3}^{\,2}}{P_{N_2} P_{H_2}^{\,3}}$$

- Gases can be expressed in terms of pressure or concentration

Kc eq constant using concentration, M

Kp eq constant using pressure, atm

What is the relationship between Kp and Kc?

$K_p = K_c (RT)^{\Delta n}$

$\Delta n$ = moles of products – moles of reactants

*gases only!

$K_c$ is equal to 0.28 for the following reaction at 900 °C

5mol 3mol

$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$

What is Kp ?

$K_p = K_c (RT)^{\Delta n}$

$\Delta n = -2$

$K_p = 0.28 (0.08206 \times 1{,}173)^{-2}$

$3 \times 10^{-5}$

# Calculating K from equilibrium concentrations

The reaction between gaseous sulfur dioxide and oxygen (gas) produces sulfur trioxide gas.

$$2SO_{2}(g) + O_2(g) \rightleftarrows 2SO_3(g)$$

The equilibrium mixture contained 0.0500 M $SO_3$, 0.00350 M $O_2$ and 0.00300 M $SO_2$, @ 800K. Calculate $K_c$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]^1}$$

## Calculating Equilibrium concentrations continued

$$K_c = \frac{(0.0500)^2}{(0.00300)^2(0.0035)^1}$$

product favored @ eq.

version 1

$K_c = 7.94 \times 10^4$

* calculating K given all eq. [ ]

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version 2

Calculating K given only one concentration @ equilibrium

# Calculating Equilibrium Concentrations Part II

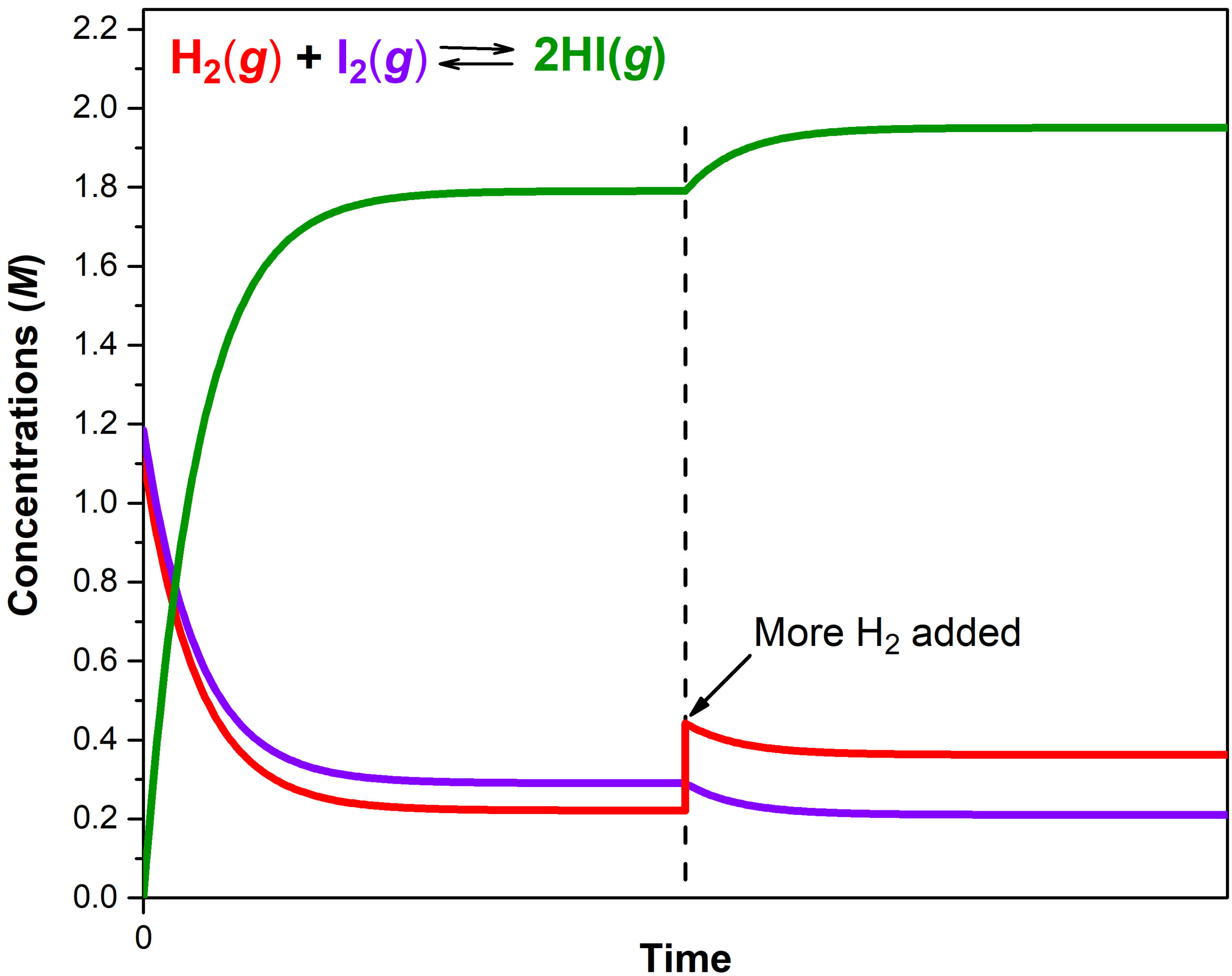
What if the initial concentration is given some reactants and products?

Need to determine the reaction quotient "Q" and the direction the reaction will shift to reach equilibrium

Calculate Q using the initial concentration of reactants and products

# Equilibrium Part III

# Le Chatelier's Principle



# Le Chateliers Principle Examples